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(71) Applicant: **SHARP CORPORATION**  
22-22, Nagaike-cho  
Abeno-ku  
Osaka 545(JP)  
Applicant: **MERCK PATENT GmbH**  
Postfach,  
Frankfurter Strasse 250  
D-64271 Darmstadt(DE)

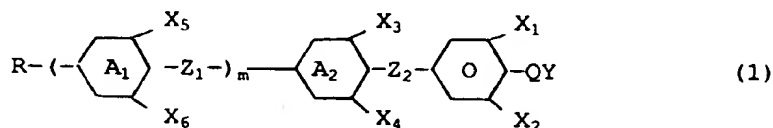
(72) Inventor: **Ohnishi, Noriaki**  
1-6-9, Veshio,  
Chuo-ku  
Osaka(JP)  
Inventor: **Hirai, Toshiyuki**  
2613-1 Ichinomotocho  
Tenri-shi, Nara Pref.(JP)  
Inventor: **Yamada, Nobuaki**

4-16 Kashi-tahon-machi  
Higashiosaka-shi, Osaka(JP)  
Inventor: **Kozaki, Shiuchi**  
51-303 2-1-2 Ukyo  
Nara-shi, Nara Pref.(JP)  
Inventor: **Coates, David**  
87 Sopwith Crescent,  
Merley  
Wimborne, Dorset BH21 3SW(GB)  
Inventor: **Brown, Emma Jane**  
77 Cranleigh Road,  
Southbourne  
Bournemouth, Dorset BH6 5JX(GB)  
Inventor: **Rieger, Bernhard**  
Hauptstrasse 31a  
D-64839 Münster-Altheim(DE)  
Inventor: **Tanaka, Yukio**  
Pure Heights Yoshimura 202,  
3-22-1, Tsumada nishi  
Atsugi-shi, Kanagawa Pref. 243(JP)

(74) Representative: **Schüttler, Reinhard, Dr.**  
Merck Patent GmbH,  
Frankfurter Strasse 250  
D-64293 Darmstadt (DE)

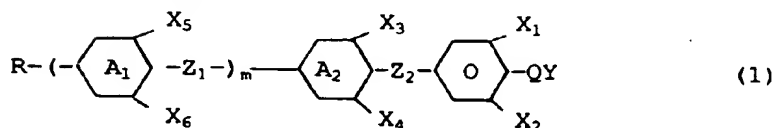
(54) Liquid crystal composite layer of dispersion type, production method thereof and liquid crystal material to be used therein.

(57) The present invention relates to a liquid crystal composite layer of polymer dispersion type in which  
(a) a liquid crystal material comprising compounds selected from the group consisting of compounds represented by the following chemical formula (1) and compounds represented by the following chemical formula (2) is dispersed in  
(b) a matrix polymer;



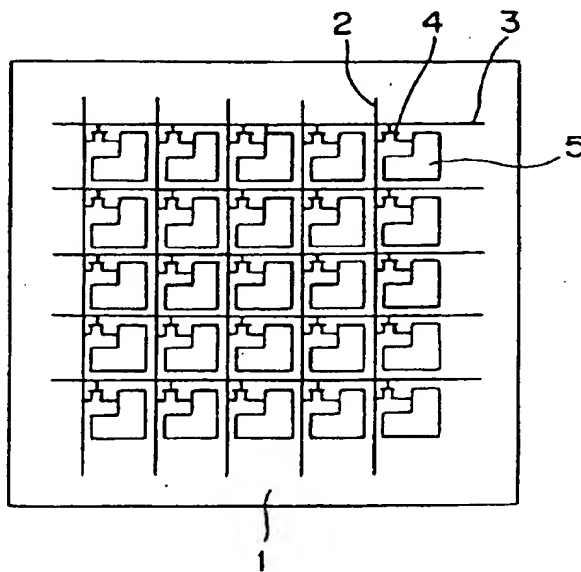
wherein

- $A_1$  and  $A_2$  represented respectively a benzene ring, cyclohexane ring, pyrimidine ring or trans-1,3-dioxane ring;  
 $X_1, X_2, X_3, X_4, X_5$  and  $X_6$  represent respectively H, F or Cl;  
 $Z_1$  and  $Z_2$  represent respectively a single bond,  $-\text{CH}_2-$ ,  $-\text{CH}_2\text{CH}_2-$ ,  $-\text{CH}=\text{CH}-$ ,  $-\text{C}\equiv\text{C}-$ ,  $-\text{COO}-$  or  $-\text{OCO}-$ ;  
 $Q$  represents a single bond,  $-\text{CH}_2-$ ,  $-\text{CH}_2\text{CH}_2-$ ,  $-\text{CF}_2-$ ,  $-\text{OCF}_2-$ ,  $-\text{C}_2\text{F}_4-$ ,  $-\text{CCl}_2-$  or  $-\text{C}_2\text{Cl}_4-$ ;  
 $Y$  represents H, F or Cl;  
 $R$  represents  $-\text{C}_n\text{H}_{2n+1}-$ ,  $-\text{C}_n\text{H}_{2n+1}\text{O}-$ ,  $-\text{C}_n\text{H}_{2n+1}\text{CH}=\text{CH}-$  (in which  $n$  represents an integer of 2-10);  
 $m$  represents 0, 1 or 2;



in which  $B$  and  $C$  represent respectively  $-\text{C}_n\text{H}_{2n+1}-$ ,  $-\text{C}_n\text{H}_{2n+1}\text{O}-$ ,  $-\text{C}_n\text{H}_{2n+1}\text{CH}=\text{CH}-$  or  $-\text{C}_n\text{H}_{2n+1}-\text{C}_6\text{H}_{10}$  (in which  $n$  is the same as mentioned above, and  $L$  is H or F).

Figure 1



Field of the invention

The present invention relates to a liquid crystal composite layer of polymer dispersion type, more specifically, to a liquid crystal composite layer of polymer dispersion type to which a display mode is applied by altering the difference of refractive index between liquid crystal droplets (or continuous liquid crystal droplets) and polymer and the directional property of the liquid crystal material by means of external voltage to control light scattering at the interface of liquid crystal/polymer.

The present invention furthermore refers to a production method of said liquid crystal composite layer and liquid crystal material to be used therein.

The liquid crystal composite layer of polymer dispersion type of the present invention can be applied to a planar display apparatus such as projection television or personal computer, a display plate to which shuttering effects are applied, a window, a door and a wall.

Background of the invention

Conventionally, display devices of TN type and STN type in which electro-optical effect is applied to nematic liquid crystal have been put into practical use. The ones constituted of liquid crystal having strong dielectric characteristics have been also proposed. These devices require a polarized light filter and an orientation treatment. On the other hand, dynamic scattering effect and phase transition effect are applied to form a liquid crystal device in which a polarized light filter is not required and scattering of liquid crystal is applied.

Recently, it has been proposed that refractive index of liquid crystal is applied to control electrically transparent conditions and white-cloudy conditions, so that a polarized light filter and an orientation treatment are not required. In this method, when voltage is applied, the orientation of liquid crystals corresponds to the direction of electrical field and the refractive index of ordinary ray of liquid crystals is made to correspond to the refractive index of polymer medium, so that the transparent conditions are formed. The light scattering conditions caused from irregular orientation of liquid crystal molecules are formed when no voltage is applied.

The method is proposed, for example, in Japanese Patent Laid-Open Sho 58-501,631 in which liquid crystals are incorporated in polymer capsules, Japanese Patent Laid-Open Sho 61-502,128 in which liquid crystal material and light-curable or heat-curable material are mixed and cured under phase separation to form liquid crystal droplets, and Japanese Patent Laid-Open Sho 59-226,322 in which a solvent is removed from a mixture of polymer and liquid crystal both of which are dissolved in the solvent to form phase-separated conditions of polymer/liquid crystals.

The liquid crystal materials used in the invention related to the references are the ones having -CN group at the end of molecular structure, such as cyano biphenyl compounds and cyano pyrimidines. Such liquid crystal materials are disclosed in Japanese Patent Laid-Open Hei 2-272,422 to 2-272,424, 2-75,688 and 2-85,822.

However, the liquid crystal compounds having -CN group at the end which are conventionally used for preparing the liquid crystal display devices of polymer dispersion type have high reactivity and tend to attract impurities in the system because of strong polarization of the -CN group. Therefore, a liquid crystal display device of polymer dispersion type having high charge holding characteristics (90 % or more) cannot be provided through conventional production processes because the liquid crystal materials are often brought into contact with the other materials. In the present application, the term "charge holding characteristics" means voltage holding ratio as is defined, for example, by S. Matsumoto et al., Liq. Cryst. 5, 1320 (1989).

In particular, in a method in which curable compounds are cured from a mixture thereof with liquid crystal compounds to separate liquid crystals from cured materials, the liquid crystals are sometimes at least partly damaged during the curing process because there exist both liquid crystal compounds and polymerizable active compounds together in one cell and the liquid crystal compounds have high reactivity. Therefore, resultant liquid crystal devices sometimes exhibit poor charge holding characteristics, which is especially true in case the liquid crystal is based on compounds with a terminal cyano group, Schiff's base LC compounds, and so on.

On the other hand, it may be thought in order to get rid of the hysteresis that a photocurable resin which can form surface or low energy is added. However, because such a resin is different in SP value (solubility parameter, see below) from that of conventional liquid crystals, the resins and the liquid crystals are not soluble in each other, so that they could not be put into a practical use.

In the method in which liquid crystals and photo curable resins are mixed uniformly and then phase-separated by photopolymerization, there is a step of mixing the liquid crystal materials with the photocurable resins. Therefore, when the compatibility between the liquid crystal materials and the resins is poor, it is necessary to raise the mixing temperature in order to uniform LC and resin mixture. When photopolymerization is carried out at such a high temperature to separate phases, the polymerization speed becomes high, so that the phase separation is started in nearly isotropic phase conditions. Therefore, dispersion particles of liquid crystals become small and as a result, high driving voltage is required.

The present invention has been achieved in consideration of above circumstances.

An object of the present invention is to provide a liquid crystal composite layer of polymer dispersion type which can meet all the most important requirements for the liquid crystal display devices of polymer dispersion type, i.e. low driving voltage, high contrast and high charge holding characteristics.

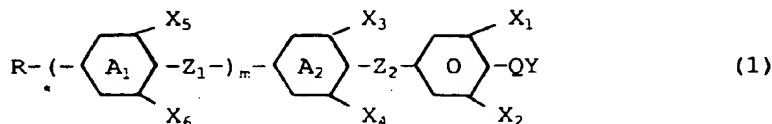
Another object of the present invention is to provide a liquid crystal optical device constituted of a liquid crystal composite layer of polymer dispersion type.

Another object of the present invention is to provide a liquid crystal material which does not exhibit the short-comings of conventional materials based on compounds with a terminal cyano group and does not undergo no degradation or degradation only to an acceptable degree when preparing the liquid crystal composite layer of the present invention via photopolymerization.

Another object of the present invention is to provide a method for preparing said liquid crystal composite layer.

## Summary of the Invention

The present invention relates to a liquid crystal composite layer of polymer dispersion type, in which (a) a liquid crystal material comprising compounds selected from the group consisting of compounds represented by the following chemical formula (1) and compounds represented by the following chemical formula (2) is dispersed in (b) a matrix polymer;



wherein

- |  |   |
|--|---|
| <p>A<sub>1</sub> and A<sub>2</sub></p> <p>X<sub>1</sub>, X<sub>2</sub>, X<sub>3</sub>, X<sub>4</sub>, X<sub>5</sub> and X<sub>6</sub></p> <p>Z<sup>1</sup> and Z<sup>2</sup></p> <p>Q</p> <p>Y</p> <p>R</p> <p>m</p> | <p>represent respectively a benzene ring, cyclo-hexane ring, pyrimidine ring or trans-1,3-dioxane ring;</p> <p>represent respectively H, F or Cl;</p> <p>represent respectively a single bond, -CH<sub>2</sub>CH<sub>2</sub>-, -CH=CH-, -C≡C-, -COO- or -OCO-;</p> <p>represents a single bond, -CH<sub>2</sub>-, -CH<sub>2</sub>CH<sub>2</sub>-, -CF<sub>2</sub>-, -OCF<sub>2</sub>-, -C<sub>2</sub>F<sub>4</sub>-, -CCl<sub>2</sub>- or -CCl<sub>2</sub> or -C<sub>2</sub>Cl<sub>4</sub>-;</p> <p>represents H, F or Cl;</p> <p>represents -C<sub>n</sub>H<sub>2n+1</sub>-, -C<sub>n</sub>H<sub>2n+1</sub>O-, -C<sub>n</sub>H<sub>2n+1</sub>CH=CH- (in which n represents an integer of 2-10);</p> <p>represents 0, 1 or 2;</p> |
|--|---|



in which

- B and C represent respectively -C<sub>n</sub>H<sub>2n+1</sub>-, -C<sub>n</sub>H<sub>2n+1</sub>O-, -C<sub>n</sub>H<sub>2n+1</sub>CH=CH- or -C<sub>n</sub>H<sub>2n+1</sub>-C<sub>6</sub>H<sub>10</sub> (in which n is the same as above mentioned), and

L is H or F.

The invention furthermore relates to a liquid crystal material comprising compounds selected from the group consisting of compounds represented by chemical formula (1) and compounds represented by chemical formula (2) at the content of 50-100 percents by weight.

5 The invention furthermore relates to a method of production of liquid crystal composite layer of polymer dispersion type, in which phases of liquid crystals are separated from a solution or a mixture of:

(a) a liquid crystal material comprising compounds selected from the group consisting of compounds represented by formula (1) and compounds represented by formula (2) at the content of 50-100 percents by weight,

10 (b) a matrix polymer and

(c) a common solvent of the liquid crystal material and the matrix polymer; if desired.

The invention furthermore relates to a method of production of liquid crystal composite layer of polymer dispersion type, in which

15 (a) a liquid crystal material comprising compounds selected from the group consisting of compounds represented by formula (1) and compounds represented by formula (2) at the content of 50-100 percents by weight, is mixed uniformly with

(b) a radical photopolymerizable resin material having average solubility parameter (SP) of 8-11 and average molecular weight (Mn) of 100-1000,

20 followed by phase separation of the liquid crystal material by photopolymerization of the polymerizable resin material;

#### Brief Explanation of Figures

25 Fig.1: A plan schematic view of one of embodiments of liquid crystal display device to which a liquid crystal composite layer of polymer dispersion type of the present invention can be applied.

Fig. 2: A sectional schematic view of one of embodiments of liquid crystal display device.

Fig. 3: A circuit for measuring apparatus of keeping characteristics.

30 Explanation of Reference number:

1. first transparent insulating substrate
2. signal line
3. scanning line
- 35 4. switching transistor
5. pixel (picture element) electrode for display
6. second transparent insulating substrate
7. counter electrode
8. liquid crystal layer
- 40 9. seal
10. driving circuit
11. transistor (FET;  $V_S$ ,  $V_G$  and  $V_D$  are source, gate and drain voltages, respectively)
12. operational amplifier
13. recorder
- 45 14. pixel (picture element) of the liquid crystal-cell

#### Detailed description of the invention

The liquid crystal compounds of the chemical formula (1) are particularly excellent in chemical stability. 50 Liquid crystal materials become more stable as these compounds are contained more. But, when the liquid crystal materials are composed only of these compounds of formula (1), the anisotropy of refractive index ( $\Delta n$ ) which is closely related to contrast of a liquid crystal display device of polymer dispersion type, can become low. In order to give high anisotropy of refractive index ( $\Delta n$ ) to liquid crystal materials, the liquid crystal compounds represented by the chemical formula (2) are added. These compounds of chemical 55 formula (2) are excellent in chemical stability, do not have highly polar groups and effect to make anisotropy of refractive index ( $\Delta n$ ) high. But, these compounds of chemical formula (2) wherein both B and C are dielectrically neutral terminal groups tend to increase the melting point and lower the dielectrical anisotropy so that the content of the liquid crystal compounds according to formula (2) is preferably chosen to be 30

% by weight or less on the basis of the total amount of liquid crystal materials.

In the present invention, other liquid crystal compounds may be mixed. In the case, the content of the liquid crystal compounds of formulae (1) and (2) is adjusted to 50-100 % by weight, preferably 70-100 % by weight, preferably 70-100 % by weight on the basis of the total amount of liquid crystal materials in order to prevent the charge holding characteristics of a liquid crystal display device of polymer dispersion type from deterioration.

Further, the compounds represented by the formulas (1) and (2) are preferably at a ration (formula (1) : formula (2)) of 100:0 to 70:30, more preferably to 80:20 and, in particular, to 95:5.

Conventional liquid crystal compounds such as cyano biphenyl compounds and cyano pyrimidines can be used as liquid crystal compounds other than the liquid crystal compounds of formulas (1) and (2).

Liquid crystal materials used should be purified sufficiently so that the liquid crystal materials may have a specific resistance of  $10^{12}$   $\Omega$ cm or more, preferably  $10^{13}$   $\Omega$ cm after preparation of the liquid crystal materials.

Among the compounds represented by formula (1), anisotropy of refractive index ( $\Delta n$ ) become higher with an increase of number of rings (N) in particular when the number of aromatic rings like 1,4-phenylene or other aromatic rings is increased.

But, when the compounds having the number of ring (N) of 4 or more are used, the clearing point of overall liquid crystal is made so high that processing characteristics are deteriorated and TCN (phase transition point of crystallization point-nematic point) is raised. Therefore, the mixing ratio need to be adjusted so that the suitable temperature range of nematic phase may be obtained.

On the other hand, as the compounds having the number of ring (N) of 2 or less make anisotropy of refractive index ( $\Delta n$ ) low, these compounds cannot be also added so much. Accordingly, preferably liquid crystal materials contain the compounds having three rings, in particular three of benzene rings and/or cyclohexane rings, in the molecular structure among the compounds represented by the formulas (1) and (2) at a content of 60 % by weight or more, preferably 80 % by weight.

The compounds according to formulae (1) and (2) are prepared by methods which are known per se, such as are described in the literature (for example in the standard works, such as Houben-Weyl, Methoden der Organischen Chemie [Method of Organic Chemistry], Georg Thieme Verlag, Stuttgart), and in particular under reaction conditions which are known and suitable for the reactions mentioned. Variants which are known per se and are not mentioned in more detail here, can also be used in this connection.

Further, cholesteric liquid crystals, dopants, dichroic dyes and other desired additives may be added so far as the chemical stability of liquid crystal materials of the present invention is not deteriorated.

For example, the adequate addition of cholesteric liquid crystals makes it possible to control selective reflection, transparency and scattering conditions of light corresponding to spiral pitches by ON-OFF electric field when the cholesteric liquid crystals have spiral pitches equal to those of visible light.

When dichroic dyes having a dichroic ratio of at least of 5, preferably 6 or more and maximum absorbing wavelength of visible light of 500 nm or more is dispersed, the lowering of light scattering ability can be restrained in the range of long wavelength and that a liquid crystal composite layer of polymer dispersion type excellent in contrast in all visible wavelength region can be formed. The compensation resulted by absorbing effects of dichroic dyes makes it possible to improve light scattering ability in all visible light region. The dichroism means characteristics to show anisotropy when a pigment molecule absorbs visible light in major axis direction and minor axis direction. When the dichroic ratio is positive, the molecule has large transition moment of light absorbance in the major axis direction of the molecule. A dichroism pigment means a pigment to show such characteristics as above mentioned.

A dichroic dye may be selected from conventional ones having characteristics as above mentioned. In embodiment, merocyanines, anthraquinones, styrenes, azobenzenes may be selected adequately.

An addition amount of the dichroic dye is within the range of 0.5 % - 10 %, preferably 1 % - 5 % in weight ratio on the basis of liquid crystal materials. A pigment may be used not only to apply the light absorbing effects to the improvement of the contrast but also to apply pigment effects to improve color quality.

The liquid crystal composite materials according to the present invention can be prepared according to known techniques.

For example, there can be used a method in which liquid crystal materials and photo-curable or heat-curable resin materials are mixed followed by phase-separation and forming of liquid crystal droplets in a polymer matrix, or a method in which a solvent is removed from a mixture of polymer and liquid crystal materials both of which are dissolved in the solvent to form separated phases of polymer/liquid crystals. Among these methods, the present invention is particularly effective to a method in which

(a) a liquid crystal material comprising compounds selected from the group consisting of compounds represented by chemical formula (1) and compounds represented by chemical formula (2) at the content of 50-100 percents by weight,  
is mixed uniformly with

- 5 (b) a radical photopolymerizable resin material having an average solubility parameter (SP) of 8-11 and an average molecular weight (Mn) of 100-1000,  
followed by phase separation of the liquid crystal material by photopolymerization of the polymerizable resin material.

Radical photopolymerizable resin materials means a photopolymerizable mixture of compounds selected from monofunctional monomers, polyfunctional monomers and oligomers thereof in the present invention. The polymerizable resin materials meets the specified SP (solubility parameter) value and molecular weight as described below. A mixing ratio of monomer components with oligomer components is so important that the temperature of compatibility thereof with liquid crystal materials is decisive.

Preferable resin materials have the chemical formula (solubility parameter value (SP)) matching to that of the above liquid crystal materials. If the SP value of the resin materials is much different from that of liquid crystal materials, the compatibility of liquid crystal with resin becomes poor, so that the mixing temperature must be raised for forming uniform conditions. When phase separations are induced by photopolymerization at high temperature, the polymerization speed becomes high, so that the phase separation is started in nearly isotropic phase conditions. Therefore, droplets of liquid crystals become small and as a result, high driving voltage is required. Preferable SP value of radical photopolymerizable resin is 8-11, more preferably 9-10 because the liquid crystal materials above mentioned have SP values of about 9.5.

The SP value in the present invention is calculated according to the following formula generally known as Fedors method:

$$\delta = \sqrt{(\sum \Delta_{ei} / \sum \Delta_{vi})}$$

in which  $\Delta_{ei}$  represents evaporation energy of atoms or atomic groups and  $\Delta_{vi}$  represents molar volume of atoms or atomic groups.

When several kinds of resins are used in combination, the SP value of the mixed resins is defined via the following formula:

$$\delta = (X_1 \cdot \delta_1 + X_2 \cdot \delta_2 + X_3 \cdot \delta_3 + \dots + X_n \cdot \delta_n) / 100$$

in which  $X_n$  represents one of % by weight of a resin component and  $\delta_n$  represents one of a SP value of the resin component.

A molecular weight of radical photopolymerizable resin materials has important influences on a temperature for mixing uniformly liquid crystal materials with resin materials. For example, in the case of photopolymerizable oligomers, different molecular weight has almost no influences on the SP value. However, the enthalpy of the molecule becomes small as the molecular weight becomes large. As a result, the solubility thereof to liquid crystals becomes so low to raise temperature for forming uniform mixture. Therefore a molecular weight of polymerizable resin materials is preferably within the range of 100-1000. If the molecular weight is less than 100, the following problems are brought about; the ration of monofunctional monomers becomes so high that resin materials are not cured sufficiently; polymerizable resin materials have so high vapor pressure that it becomes difficult to pour the materials into a cell under vacuum and toxicity becomes so high that industrial production becomes difficult. If the average molecular weight is more than 1000, a temperature for forming isotropic phase with liquid crystals becomes so high that it is inevitable that polymerization speed becomes high. As a result, dispersion particles size of formed liquid crystals becomes so small that high driving voltage is required. More preferably average molecular weight is within the range of 150-300.

Molecular weight ( $M_0$ ) of oligomers in the present invention means average molecular weight obtained by means of gel permeation chromatography on the basis of standard poly(methyl methacrylate) (PMMA) of monodispersion type.

Average molecular weight of a mixture of compounds having different chemical structures is defined as the following formula:

$$M = (X_1 \cdot M_1 + X_2 \cdot M_2 + X_3 \cdot M_3 + \dots + X_n \cdot M_n) / 100$$

in which  $X_n$  represents a % by weight of resin component and  $M_n$  represents an average molecular weight of single component itself before mixing.

In particular, monofunctional monomers are contained in polymerizable resin materials at a content 60-98 %, preferably 80-90 %. If the content is less than 60 %, the following problems are brought about. The molecular weight of polymerizable resin materials are increased, so that the compatible temperature of liquid crystals and resin materials are raised. Moreover polyfunctional monomers accelerate the speed of phase separation of liquid crystal molecules/polymers because the polyfunctional monomers effect great growth of crosslinked structure. If the content is more than 98 %, polymer matrix having sufficient strength cannot be formed. Particle size of liquid crystal dispersions becomes very large because sufficient phase separation speed cannot be obtained. Accordingly, the contrast of a resultant cell is remarkably deteriorated.

A content of the polyfunctional monomers is within the range of 5-25 % by weight, preferably 8-15 % by weight, most preferably about 10 % by weight.

A content of the oligomers is within the range of 5-20 % by weight, preferably 8-15 % by weight.

With respect to monomers constituting polymerizable resin materials, acrylic acids and acrylates may be the ones having alkyl groups or benzene rings in which the benzene rings, the alkyl groups (straight or branched) or hydrogen atoms are substituted partially or all by halogen atoms such as fluorine and chlorine.

More concretely, monofunctional monomers are exemplified by isobutyl acrylate, stearyl acrylate, lauryl acrylate, isoamyl acrylate, n-butyl methacrylate, n-lauryl methacrylate, tridecyl methacrylate, n-stearyl methacrylate, cyclohexyl methacrylate, benzyl methacrylate, 2-ethylhexyl acrylate, 2-phe-noxyethyl methacrylate, bisphenol-A-dimethacrylate, bisphenol-A-diacylate.

Polyfunctional monomers work to improve physical strength of polymer and are exemplified by dimethacrylate of 1,4-butanediol, dimethacrylate of 1,6-hexanediol, trimethacrylate of trimethylolpropane, triacrylate of trimethylolpropane and tetra-acrylate or tetramethylolmethane.

It is more preferable that the monomers mentioned above are fluorinated or chlorinated. These halogenated compounds work to make the interaction at interface between liquid crystal materials and resins low and to get rid of hysteresis effectively. A content of the fluorinated or chlorinated monomers is preferably 0.1-50 % by weight of the total polymerizable resin materials. If the content is less than 0.1 % by weight, the effect to get rid of hysteresis is small. The addition of more than 50 % by weight is not practical because the temperature for compatibility becomes high on account of large difference of SP values between the halogenated monomers and the other monomers. Fluorinated or chlorinated compounds are exemplified by 2,2,3,4,4,4-hexafluorobutyl methacrylate, 2,2,3,4,4,4-hexachlorobutyl methacrylate, 2,2,3,3-tetrafluoropropyl methacrylate, 2,2,3,3-tetrafluoropropyl methacrylate, perfluorooctylethyl methacrylate, perfluorooctylethyl methacrylate, perfluorooctylethyl acrylate, perchlorooctylethyl acrylate.

Oligomers are exemplified by urethane-acrylate and poly(oxyethylene-acrylate).

In the preparation of liquid crystal composite layers of dispersion type, liquid crystal materials, radical photopolymerizable resin materials, photopolymerization initiators and other desired additives are mixed uniformly at a specified content to prepare prepolymers. In this case, a content of the liquid crystal materials is within the range of 95-60 % by weight, preferably 90-80 % by weight on the basis of the photopolymerizable resin materials.

With respect to the photopolymerization initiators, the conventional ones may be used. A content of photopolymerization initiators is preferably within the range of (1-5 %) by weight, preferably (2-4 %) by weight on the basis of the photopolymerizable resin materials.

The other desired additives which may be added are exemplified by solvents.

Prepolymers (which may contain a solvent) used for production of a liquid crystal display device of polymer dispersion type should be highly purified because of the direct contact thereof with liquid crystal materials. In particular, non-reacted materials, synthetic catalysts, decomposition products of the prepolymers and water are removed sufficiently. Concretely speaking, prepolymer is adjusted to have resistant value of  $10^{11}$   $\Omega$ cm or more, preferably  $10^{12}$   $\Omega$ cm or more, so that characteristics of the present invention can be made best use of.

A liquid crystal composite layer of polymer dispersion type is prepared by pouring the polymer into a desired cell or device, followed by irradiation for photopolymerization of radical photopolymerizable resin to separate phases of liquid crystal materials from the resins.

The conditions for photopolymerizable are typically as follows:

kind of light:	high pressure mercury lamp
strength of light:	30 ~ 50 mW/cm <sup>2</sup>
irradiation time:	60 seconds

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The liquid crystal composite layer of dispersion of the present invention can further be prepared by applying a mixed solution of a liquid crystal material and a matrix polymer having optically uniform characteristics in a common solvent by a casting method and then drying to form separated phases of the liquid crystals in the matrix polymer. A liquid crystal panel of polymer dispersion type prepared as mentioned above has relatively excellent charge holding characteristics at high voltage and stability because the liquid crystal material is highly stable and a production process of the composite layer of liquid crystal/polymer does not accompany chemical reaction. Especially large display panels can be prepared by this method.

A method of this type has been recently reported in Polymer preprints Japan, vol. 37, No. 8 (1988), Japanese Patent Laid Open Sho 59-226322 or Japanese Patent Laid Open Hei 1-250,925. According to these references, a polymer and a liquid crystal material are dissolved in a solvent, the obtained solution is applied on a transparent plate by a casting method and dried and then a counter transparent electrode is laminated to form a liquid crystal panel. According to this method, the obtained composite layer is constituted of matrix polymer having spongy constitution and crystals liquid which fill the pores of the polymer in spherical forms or continuous forms.

This preparing method of the liquid crystal-polymer composite layer is advantageous in that a chemical reaction is not accompanied in a process of phase separation and that a large display can be formed. These advantages can often not be obtained in a preparing method in which phase separation is carried out by a heat polymerization or light polymerization method in a uniform solution containing thermosetting monomers, photopolymerizing monomers and liquid crystal materials, unless liquid crystal materials and radical photopolymerizable resin materials are properly and carefully adjusted to each other as was described above.

Matrix polymers used for production of a liquid crystal composite layer of polymer dispersion type should be highly purified because of the direct contact thereof with liquid crystals, have high uniformity and are excellent in transparency. Concretely speaking, the matrix polymer is adjusted to have resistant value of  $10^{12}$   $\Omega$ cm or more, preferably  $10^{13}$   $\Omega$ cm or more, so that the characteristics of liquid crystal materials of the present invention can be made best use of.

An operating mode of a display device constituted of a liquid crystal composite layer of dispersion type changes with the response of refractive index of liquid crystals dispersed in matrix polymer to electrical field. Light transmittable conditions in which the refractive index is almost equal to that of matrix polymer ( $n_p$ ) and light scattering conditions in which refractive indices of liquid crystal/matrix polymer is not in harmony are controlled. Therefore, it is desirable to select a matrix polymer having a refractive index ( $n_p$ ) which is related with the refractive index of ordinary ray of the liquid crystal material ( $n_o$ ) by the formula:

$$|n_o - n_p| < 0.2$$

A matrix polymer may be selected from the ones satisfying the characteristics above mentioned and being soluble in a solvent. Such a polymer is exemplified by synthetic resins, synthetic rubbers or natural rubbers such as a vinyl chloride resins, carbonate resins, methacrylate resins, fluorine resins, silicone resins, acrylic resins, styrene resins, vinyl resins and hydrolized compounds thereof, nitrile resins, amide resins.

In preparation of a liquid crystal composite layer of dispersion type, a mixing ratio in weight (liquid crystal material: matrix polymer) is adjusted within the range of 95 : 5 - 30 : 70, preferably 90 : 10 - 60 : 40 so that light-transmittance may be made as small as possible when no voltage is applied and that the contrast may be made high.

A common solvent of liquid crystal material and matrix polymer is exemplified by chloroform etc.

The specific choice of the solvent and the coating and drying conditions depends on each liquid crystal and resin material and can be optimized by the expert without any inventive effort.

A liquid crystal composite layer of polymer dispersion type of the present invention may be applied to, for example, liquid crystal display device as shown in Fig. 1 and Fig. 2. The liquid crystal composite layer of polymer dispersion type (8) is interposed as a liquid crystal layer between an electrode for display and a counter electrode in the device. A pixel (picture element) electrode (5), a switching transistor (4) matching to the electrode (5) and path lines such as a signal line (2) and a scanning line (3) are arranged in a matrix form on a transparent and insulating substrate (1) made of glass having no birefringence to give a display

electrode substrate for active matrix driving system. As the switching transistor (4), an a-Si thin film transistor (TFT) is formed. The counter electrode (7) is formed on a transparent insulating substrate (6) made of a glass oppositely to each pixel (picture element) electrode (5). The picture element electrode (5) and the counter electrode (7) are transparent electrodes for applying voltage to the liquid crystal layer (8).  
5 The liquid crystal layer (8) is sealed with a seal (9) made of epoxy resin.

The present invention is explained by concrete examples hereinafter. The scope of the invention, however, is not limited by the concrete examples.

According to the present invention, the use of chemically stable liquid crystal compounds of F and Cl series effects to improve the charge holding characteristics which were most serious problem in a liquid  
10 crystal display device of polymer dispersion type.

Liquid crystal materials of the present invention can provide a liquid crystal display device of polymer dispersion.

According to the present invention, the combination of chemically stable liquid crystal compounds of F and Cl series with carefully chosen polymerizable resin materials suitable for the liquid crystal material or  
15 with a matrix polymer (typically in a common solvent), can provide a liquid crystal display device of polymer dispersion type having improved charge holding characteristics which were most serious problem in a liquid crystal display device of polymer dispersion type, and display characteristics excellent in low driving voltage, high contrast, low hysteresis and high reliability.

#### 20 **Example 1**

Liquid crystal material A of 2 g shown in Table 1 was mixed with poly (methyl methacrylate) (PMMA) (Derupet (trade name); made by Asahi Kasei Kogyo K.K.) of 0.5 g. The obtained mixture was dissolved uniformly in chloroform as a common solvent to give a solution of solute content of 15 wt%. The uniform  
25 solution was applied by a bar-coat method onto ITO glass (on the surface of which indium oxide and tin oxide were deposited) (FLINT GLASS with ITO of 500 Å made by Nippon Ito Glass K.K.) so that a uniform composite layer of liquid crystal/polymer of 13-15 μm might be formed after drying. Then, a counter electrode made of transparent glass with electrically conductive layer thereon, was laminated. Then, the polymer composite layer was sealed. Thus, a liquid crystal display cell of polymer dispersion type was  
30 obtained.

35

40

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50

55

Table 1

composition of liquid crystal material	content (%)
	20
	20
	20
	15
	15
	5
	5
clearing point (centigrade)	94
anisotropy of refractive index	0.1944

Charge holding characteristics of the resultant cell were measured by means of a system for measuring the charge holding characteristics shown in Figure 3. The system is constituted of a switching transistor (FET, 11) which works to apply voltage to electrodes, a driving circuit (10) and a circuit for measuring discharge of electrical charges (13) in the cell (14). The charge holding characteristics were measured at room temperature. The results are shown in Table 4.

Threshold voltage ( $V_{th}$ ) and saturated voltage ( $V_s$ ) were measured as electro-optic characteristics of the prepared cell. The threshold voltage ( $V_{th}$ ) means the value of voltage at the time when light transmittance is increased by 10 % on the basis of the difference between saturated light transmittance ( $T_s$ ) and light transmittance ( $T_o$ ) when no voltage is applied. Light transmittance ( $T_s$ ) or ( $T_{100}$ ) means the value at the time when saturation voltage is applied to the cell. Light transmittance ( $T_o$ ) means the value at the time when no voltage is applied to the cell. The cell displayed  $V_{th}$  of 6.2 V and  $V_s$  of 8.1 V. The driving voltage was very low when compared with that of conventional cells and response characteristics were excellent.

The prepared cell had transmittance of light of direct view of 3.5 % at no voltage and 79.1 % at 50 V of alternating voltage applied when collecting angle is  $6^\circ$  at light receiving portion. Contrast was excellent.

#### Example 2, 3 and Comparative Examples 1, 2

Liquid crystal display devices of polymer dispersion type were prepared in a manner similar to that of Example 1, except that liquid crystal material B shown in Table 2 (Example 2), liquid crystal material C shown in Table 3 (Example 3), liquid crystals of cyano biphenyl compounds (made by E. Merck, Germany; Comparative Example 1), E44 (made by E. Merck, Germany; Comparative Example 2) were used instead of the liquid crystal material A in Example 1.

Charge holding characteristics of the obtained cells were measured in a manner similar to that of Example 1. The results are shown in Table 4 (see below of Example 4).

Table 2

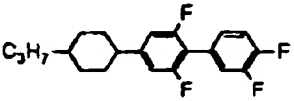
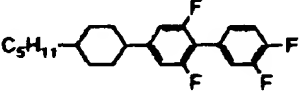
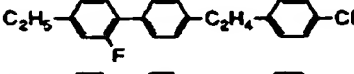
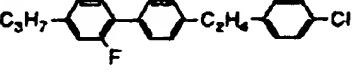
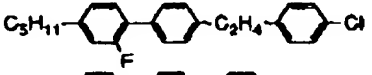
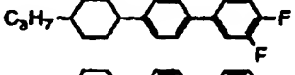
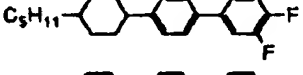
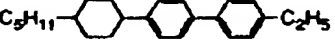


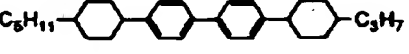































composition of liquid crystal material	content (%)
	5
	5
	15
	15
	15
	13
	13
	5
	5
	3
	3
	3
clearing point (centigrade)	110
anisotropy of refractive index	0.1739

Table 3

composition of liquid crystal material	content (%)
$C_5H_{11}$ -  - 	5
$C_7H_{15}$ -  - 	6
$C_3H_7$ -  - 	6
$C_5H_{11}$ -  - 	6
$C_3H_7$ -  -  - $C_2H_4$ - 	12
$C_5H_{11}$ -  -  - $C_2H_4$ - 	18
$C_3H_7$ -  - 	12
$C_5H_{11}$ -  - 	12
$C_3H_7$ -  - 	5
$C_5H_{11}$ -  - 	5
$C_5H_{11}$ -  - 	4
$C_3H_7$ -  -  - $C_3H_7$	3
$C_5H_{11}$ -  -  - $C_3H_7$	3
$C_5H_{11}$ -  -  - $C_5H_{11}$	3
clearing point (centigrade)	99
anisotropy of refractive index	0.1571

## Example 4

Dichroic dye D37 (anthraquinone type) (made by Merck Ltd., Great Britain) having maximum absorbing wavelength at 556 nm was further added at 3 wt% to the liquid crystal material in Example 1 to prepare a liquid crystal display device of polymer dispersion type in a manner similar to the above Examples and Comparative Examples.

The prepared cell was colored because visible lights are absorbed by the added dye. The prepared cell had transmittance of light of direct view of 3.0 % at no voltage and 78.5 % at 50 V of alternating voltage applied when collecting angle is 6° at light receiving portion. Contrast was somewhat improved further.

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The charge holding characteristics were measured in a manner similar to Example 1. The results are shown in Table 4.

Table 4

keeping characteristics (%)					
Ex. 1	Ex. 2	Ex. 3	Ex. 4	Com. Ex. 1	Com. Ex. 2
98.6	98.4	98.7	92.5	82.1	83.8

## Example 5

Liquid crystal compounds of 2 g shown in Table 1 were added to resin mixture of 2-ethylhexyl acrylate of 0.4 g, diacrylate of neopentylglycol of 0.05 g and oligomer of urethane acrylates of 0.05 g. Further, photocuring agent (Irgacure 184; made by Ciba Geigy, Switzerland) of 0.02 g was mixed to give uniform solution at 40 °C. A spacer was interposed to form a cell having 12 μm space between two plates of ITO glass (on the surface of which indium oxide and tin oxide were deposited) (FLINT GLASS with ITO of 500 Å made by Nippon Ito Glass K.K.). The mixture obtained above was poured into the cell. Then the cell was irradiated by high pressure mercury lamp at power of 30 mW/cm<sup>2</sup> (irradiation strength of ultraviolet of 365 nm) at room temperature for 2 minutes to cure resins.

Charge holding characteristics, threshold voltage (V<sub>th</sub>), saturation voltage (V<sub>s</sub>) and light transmittance T<sub>s</sub> respectively T<sub>o</sub> were measured as described in example 1.

The following results were obtained:

Keeping characteristic (room temperature)	98.2 %
V <sub>th</sub>	2.6 V
V <sub>s</sub>	5.7 V
T <sub>o</sub>	2 % (0 V)
T <sub>s</sub>	82.1 % (50 V)

## Examples 6, 7 and Comparative Examples 3, 4

Liquid crystal display devices of polymer dispersion type were prepared in a manner similar to that of Example 5, except that liquid crystal materials shown in Table 2 (see Example 2), liquid crystal materials shown in Table 3 (see Example 3), liquid crystals of cyano biphenyl compounds (made by E. Merck, Germany; Comparative Example 1), E44 (made by E. Merck, Germany; Comparative Example 2) were used.

Charge holding characteristics of the obtained cells were measured in a manner similar to that of Example 1. The results are shown in Table 5.

Table 5

Charge holding characteristics (%)				
Ex. 5	Ex. 6	Ex. 7	Com. Ex. 3	Com. Ex. 4
98.2	98.1	98.5	85.2	87.4

## Examples 8, 9 and 10

2-ethylhexyl acrylate (2EHA; SP value : 8.6, average molecular weight (Mn) : 1984, specific resistance of liquid : 1.2 x 10<sup>12</sup> Ωcm; made by Nippon Kayaku K.K.) and diacrylate monomer (R-684; SP value : 10.3, average molecular weight (Mn) : 304, specific resistance of liquid : 2.1 x 10<sup>12</sup> Ωcm; made by Nippon Kayaku K.K.) were mixed at a ration as shown in Table 6 to give a radical photopolymerizable resin material.

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Average molecular weights and SP values of the prepared polymerizable resin material are also shown in Table 6.

Table 6

Example No.	Content of 2EHA (%wt)	Content of R-684 (%wt)	SP value	Average Molecular Weight (Mn)
8	93	7	8.74	192
9	90	10	8.79	196
10	80	20	8.96	208
Com. Ex. 5	99	1	8.64	185
Com.Ex. 6	50	50	9.46	244

These polymerizable resin materials of 0.3 g, liquid crystal materials A (made by E. Merck, Germany) shown in Table 1 (see Example 1) of 1.2 g and photoinitiator (Irgacure 184; made by Ciba Geigy, Switzerland) of 0.045 g were mixed uniformly at 80 °C.

A spacer was interposed to form a cell having 12 μm space between two plates of ITO glass (on the surface of which indium oxide and tin oxide were deposited) (FLINT GLASS with ITO of 500 Å made by Nippon Ito Glass K.K.). The mixture obtained above was poured into the cell. Then the cell was irradiated by low pressure mercury lamp at a power of 50 mW/cm<sup>2</sup> (irradiation strength of ultraviolet of 365 nm; UV illumination photometer UIT-101; made by Ushio Denki K.K.) at irradiation temperature of 15 °C for 20 seconds to polymerize and cure the resin materials. After UV irradiation, the cell was left for 2 hours at 50 °C.

Charge holding characteristics, threshold voltage ( $V_{th}$ ), saturation voltage ( $V_s$ ) and values of light transmittance  $T_s$  (50 V) ( $T_s = T_{100}$ ) respectively  $T_o$  (0 V) were measured as described in Example 1.

The results are summarized in Table 7.

Table 7

Example No.	Ex. 8	Ex 9	Ex. 10
Charge holding characteristics (%)	97.5	98.2	97.7
threshold voltage ( $V_{th}$ )	2.3	2.7	6.5
saturation voltage ( $V_{sat}$ )	4.2	5.1	11.3
light-transmittance ( $T_o$ )	6.0	2.0	1.2
light-transmittance ( $T_{100}$ )	82.8	81.5	79.8
temperature of UV irradiation (°C)	15	15	20

## Examples 11, 12 and Comparative Examples 5, 6

Liquid crystal display devices of polymer dispersion type were prepared in a manner similar to that of Example 8, except that liquid crystal materials B shown in Table 2 (see Example 2), liquid crystal materials C shown in Table 3 (see Example 3), liquid crystals of cyano biphenyl compounds (made by E. Merck, Germany; Comparative Example 1), E44 (made by E. Merck, Germany; Comparative Example 2) were used.

The charge holding characteristics of the obtained cells were measured in a manner similar to that of Example 1. The results are shown in Table 8.

Table 8

Example No.	Ex. 11	Ex. 12	Com. Ex. 5	Com. Ex. 6
charge holding characteristics (%)	96.6	97.5	85.1	83.8
threshold voltage ( $V_{th}$ )	5.8	3.1		
saturation voltage ( $V_{sat}$ )	11.0	5.3		
light-transmittance ( $T_o$ )	8.0	8.0		
light-transmittance ( $T_{100}$ )	82.3	84.4		
temperature of UV irradiation ( $^{\circ}\text{C}$ )	55	65		

In Comparative Examples 5 and 6, polymerizable resin materials and liquid crystal materials were not mixed at low temperature and the compatible temperatures were  $80^{\circ}\text{C}$  and  $85^{\circ}\text{C}$  respectively. The light transmittance of the prepared cells were hardly changed at the application voltage of 50 V, and the charge holding ratio were 85.1 % and 83.3 % respectively. The cells can hardly be put into practical use.

#### Comparative Example 7, 8

Liquid crystal display devices of polymer dispersion type were prepared in a manner similar to that of Example 8 except that resin materials having composition shown in Table 6 were prepared by use of the same compound as those of Example 8 and the liquid crystal material A (shown in Table 1) was used. The electro-optical characteristics of the obtained cells were shown in Table 9.

Table 9

Example No.	Com. Ex. 7	Com. Ex. 8
charge holding characteristics (%)	98.1	97.3
threshold voltage ( $V_{th}$ )	2.5	24.4
saturation voltage ( $V_{sat}$ )	5.0	55.6
light-transmittance ( $T_o$ )	43.0	0.5
light-transmittance ( $T_{100}$ )	82.3	80.2
temperature of UV irradiation ( $^{\circ}\text{C}$ )	10	25

#### Examples 13, 14 and 15

2-ethylhexyl acrylate (2EHA; SP value : 8.6, average molecular weight (Mn) : 184; made by Nippon Kayaku K.K.) and diacrylate monomer (R-684; SP value : 10.3, average molecular weight (Mn) : 304; made by Nippon Kayaku K.K.), oligomer of urethane acrylate (SP value : 10.3, average molecular weight (Mn) : 1700, specific resistance of liquid  $1.5 \times 10^{12} \Omega\text{cm}$ ; made by Nippon Kayaku K.K.) were mixed at a ration as shown in Table 10 to give photopolymerizable resin materials. Average molecular weights and SP values of the prepared polymerizable resin materials are also shown in Table 10.

Table 10

Example No.	Content of 2EHA (%wt)	Content of R-689 (% wt)	Content of oligomer (wt %)	SP value $\delta$	Average Molecular Weight (Mn)
13	93	5	2	8.74	220
14	90	7	3	8.79	235
15	80	14	6	8.96	292
Com. Ex. 9	60	0	40*	8.29	1110
Com. Ex. 10	100	0	0	8.64	184

The mark "\*" means that a compound having average molecular weight (M) : 2500 is used as an urethane acrylate oligomer.

Liquid crystal display devices of polymer dispersion type were prepared in a manner similar to that of Example 8 by use of the resin materials and the liquid crystal material A (shown in Table 1, see example 1). The electro-optical characteristics of the obtained cells are shown in Table 11.

Table 11

Example No.	Ex. 13	Ex. 14	Ex. 15
charge holding characteristics (%)	98.2	96.8	97.3
threshold voltage ( $V_{th}$ )	2.6	3.7	7.5
saturation voltage ( $V_{sat}$ )	5.9	5.8	9.7
light-transmittance ( $T_o$ )	8.2	1.5	0.5
light-transmittance ( $T_{100}$ )	81.9	73.2	83.1
temperature of UV irradiation ( $^{\circ}C$ )	15	15	20

#### Examples 16, 17 and 18

2-ethylhexyl acrylate (2EHA; SP value : 8.6, average molecular weight (Mn) : 184; made by Nippon Kayaku K.K.), perfluorooctylethyl acrylate (FA-108; SP value : 7.4, average molecular weight (Mn) : 574; made by Kyoeisa K.K.), diacrylate monomer (R-684; SP value : 10.3, average molecular weight (Mn) : 304; made by Nippon Kayaku K.K.) and oligomer of urethane acrylate (SP value : 10.3, average molecular weight (Mn) : 1700, specific resistance of liquid :  $1.5 \times 10^{12} \Omega cm$ ; made by Nippon Kayaku K.K.) were mixed at a ratio as shown in Table 12 to give polymerizable resin materials. Average molecular weights and SP values of the prepared resin materials are also shown in Table 12.

Table 12

Example No.	Content of 2EHA (%wt)	Content of R-689 (% wt)	Content of FA-108 (wt %)	SP value	Average Molecular Weight (Mn)
16	72	20	8	8.84	240
17	64	20	16	8.75	253
18	54	20	26	8.63	301

Liquid crystal display devices of polymer dispersion type were prepared in a manner similar to that of Example 8 by use of the resin materials and the liquid crystal material A (shown in Table 1, see Example 1). The electro-optical characteristics of the obtained cells were measured in a manner similar to Example 1. The hysteresis was evaluated by measuring the difference of the voltage between half-tone voltage  $V_{50}$  at voltage-decreasing time and  $V_{50}$  at voltage increasing time. The  $V_{50}$  means the halftone voltage at increasing/decreasing applied voltage.

Table 13

Example No.	Ex. 16	Ex. 17	Ex. 18
charge holding characteristics (%)	96.1	95.2	94.5
threshold voltage ( $V_{th}$ )	4.5	3.7	3.4
saturation voltage ( $V_{sat}$ )	9.3	6.1	6.8
hysteresis ( $V_h$ ) (V)	0.1	< 0.1	< 0.1
light-transmittance ( $T_o$ ) (%)	1.0	2.2	4.5
light-transmittance ( $T_{100}$ ) (%)	80.1	75.6	70.2
temperature of UV irradiation (°C)	20	25	25

**Comparative Examples 9 and 10**

Liquid crystal display devices of polymer dispersion type were prepared in a manner similar to that of Example 8, except that the compound having average molecular weight ( $M_n$ ) of 2500 and the same repeating units as those of the oligomer urethane acrylate used in Examples 13, 14 and 15 was used in Comparative Example 9; 2EHA (100 %) was used in Comparative Example 10 as a radical photopolymerizable resin material and the same liquid crystal materials as those of Example 1 (see Table 1) were used in respective Comparative Examples. The composition of resin materials are shown in Table 10. The electro-optical characteristics of the obtained cells are shown in Table 14.

Table 14

Example No.	Com. Ex. 9	Com. Ex. 10
charge holding characteristics (%)	96.6	96.1
threshold voltage ( $V_{th}$ ) (V)	-	-
saturation voltage ( $V_{sat}$ ) (V)	-	-
light-transmittance ( $T_o$ ) (%)	0.5	75.2
light-transmittance ( $T_{100}$ )	20.2	83.5
temperature of UV irradiation (°C)	80	5

In Comparative Example 9, the saturation voltage was 50 V or more. In Comparative Example 10, resin materials were not cured sufficiently, so that sufficient contrast could not be achieved.

**Comparative Example 11**

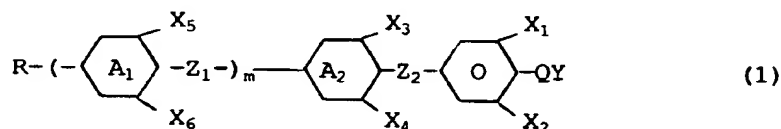
2-hydroxyethyl acrylate (Light Ester HOA; SP value : 12.5; molecular weight ( $M_n$ ); 116; made by Kyoeisya K.K.) was used instead of 2EHA used in Example 9 to be mixed with the liquid crystal material A (shown in Table 1, see Experiment 1). But, the both compounds were not mixed uniformly even at 80 °C. So a cell could not be prepared. The composition of the resin material is shown in Table 15.

Table 15

Comparative Example No.	Content of HOA (%wt)	Content of R-684 (%wt)	SP value	Average Molecular Weight ( $M_n$ )
11	95	5	12.4	125

## Claims

1. A liquid crystal composite layer of polymer dispersion type, in which  
 (a) a liquid crystal material comprising compounds selected from the group consisting of compounds  
 represented by the following chemical formula (1) and compounds represented by the following  
 chemical formula (2) is dispersed in  
 (b) a matrix polymer;



wherein

- |  |   |
|--|---|
| <p>A<sub>1</sub> and A<sub>2</sub></p> <p>X<sub>1</sub>, X<sub>2</sub>, X<sub>3</sub>, X<sub>4</sub>, X<sub>5</sub> and X<sub>6</sub></p> <p>Z<sub>1</sub> and Z<sub>2</sub></p> <p>Q</p> <p>Y</p> <p>R</p> <p>m</p> | <p>represented respectively a benzene ring, cyclohexane ring, pyrimidine ring or trans-1,3-dioxane ring;</p> <p>represent respectively H, F or Cl;</p> <p>represent respectively a single bond, -CH<sub>2</sub>-, -CH<sub>2</sub>CH<sub>2</sub>-, -CH=CH-, -C≡C-, -COO- or -OCO-;</p> <p>represents a single bond, -CH<sub>2</sub>-, -CH<sub>2</sub>CH<sub>2</sub>-, -CF<sub>2</sub>-, OCF<sub>2</sub>-, -C<sub>2</sub>F<sub>4</sub>-, -CCl<sub>2</sub>- or -C<sub>2</sub>Cl<sub>4</sub>-;</p> <p>represents H, F or Cl;</p> <p>represents -C<sub>n</sub>H<sub>2n+1</sub>-, -C<sub>n</sub>H<sub>2n+1</sub>O-, -C<sub>n</sub>H<sub>2n+1</sub>CH=CH- (in which n represents an integer of 2-10);</p> <p>represents 0, 1 or 2;</p> |
|--|---|



in which B and C represents respectively -C<sub>n</sub>H<sub>2n+1</sub>-, -C<sub>n</sub>H<sub>2n+1</sub>O-, -C<sub>n</sub>H<sub>2n+1</sub>CH=CH- or -C<sub>n</sub>H<sub>2n+1</sub>-C<sub>6</sub>H<sub>10</sub>- (in which n is the same as above mentioned, and L is H or F).

2. A liquid crystal composite layer of polymer dispersion type of Claim 1, in which the matrix polymer has an electrical resistance of  $10^{12} \Omega \text{cm}$  or more and the refractive index of the polymer matrix ( $n_p$ ) is related with the refractive index of ordinary ray of the liquid crystal material ( $n_o$ ) by the formula:

$$|n_o - n_p| < 0.2$$

3. A liquid crystal composite layer of polymer dispersion type of Claim 1, in which the matrix polymer is mixed with the liquid crystal material at a weight ratio within the range between 10:90 - 40:60.
4. A liquid crystal composite layer of polymer dispersion type of Claim 1, further comprising a dichroic dye having maximum absorbing wavelength of visible light at 500 nm or more and a dichroic ratio of at least of 5.
5. A liquid crystal composite layer of polymer dispersion type of Claim 1, in which the liquid crystal material is dispersed in the matrix polymer by means of phase separation.
6. A method of production of liquid crystal composite layer of polymer dispersion type, in which phases of liquid crystals are separated from a solution or a mixture of;  
 (a) a liquid crystal material comprising compounds selected from the group consisting of compounds represented by chemical formula (1) and compounds represented by chemical formula (2) at the

content of 50-100 percents by weight,

(b) a matrix polymer and

(c) a common solvent of the liquid crystal material and the matrix polymer, if desired.

- 5 7. A method of production of liquid crystal composite layer of polymer dispersion type, in which  
(a) a liquid crystal material comprising compounds selected from the group consisting of compounds  
represented by formula (1) and compounds represented by formula (2) at the content of 50-100  
percents by weight,  
is mixed uniformly with  
10 (b) a radical photopolymerizable resin material having average solubility parameter (SP) of 8-11 and  
average molecular weight (Mn) of 100-1000,  
followed by phase separation of the liquid crystal material by photopolymerization of the polymerizable  
resin material.
- 15 8. A method of production of liquid crystal composite layer of polymer dispersion type of Claim 7, in  
which the radical photopolymerizable resin material comprises at least a polymerizable fluorinated resin  
material.
- 20 9. A method of production of liquid crystal composite layer of polymer dispersion type of Claim 7, in  
which the radical photopolymerizable resin material is selected from monofunctional monomers,  
polyfunctional monomers and oligomers thereof, a content of the monofunctional monomers is within  
the range of 60-98 % by weight.
- 25 10. A method of production of liquid crystal composite layer of polymer dispersion type of Claim 7, in  
which the radical photopolymerizable resin material of 100 parts by weight is mixed with the liquid  
crystal material of 300-500 parts by weight.
- 30 11. A liquid crystal material comprising compounds selected from the group consisting of compounds  
represented by formula (1) and compounds represented by chemical formula (2) at the content of 50-  
100 percents by weight.
- 35 12. A liquid crystal material of Claim 11, in which among the compounds represented by the formula (1)  
and (2) the ones having three of benzene rings and/or cyclohexane rings in the molecular structure is  
contained at a content of 60 percents by weight or more.
- 40 13. A liquid crystal material of Claim 11, in which the compound represented by the formula (1) and the  
compound represented by the formula (2) is contained at a ration of 95 : 5 - 70 : 30 (formula (1) to  
formula (2)).
- 45 14. A liquid crystal display device, in which the liquid crystal composite layer of polymer dispersion type of  
Claim 1-5 is interposed between two electrodes at least one of which is transparent.

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Figure 1

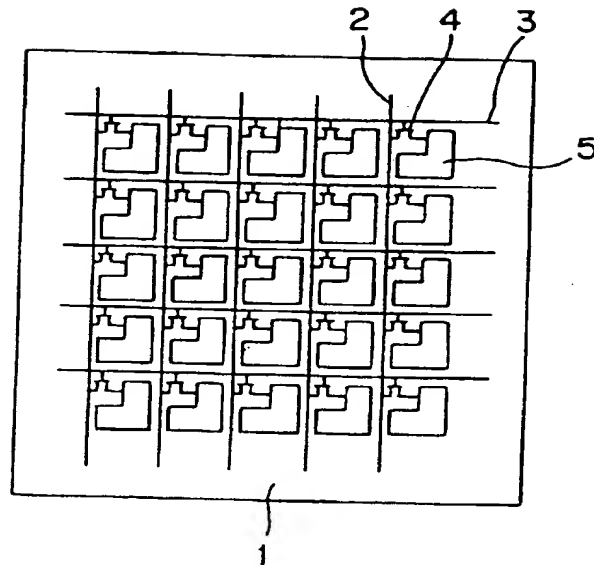


Figure 2

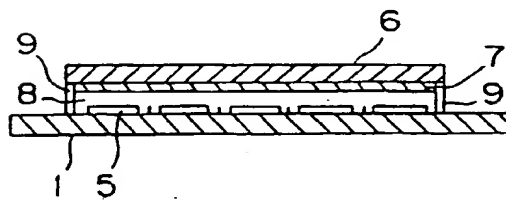
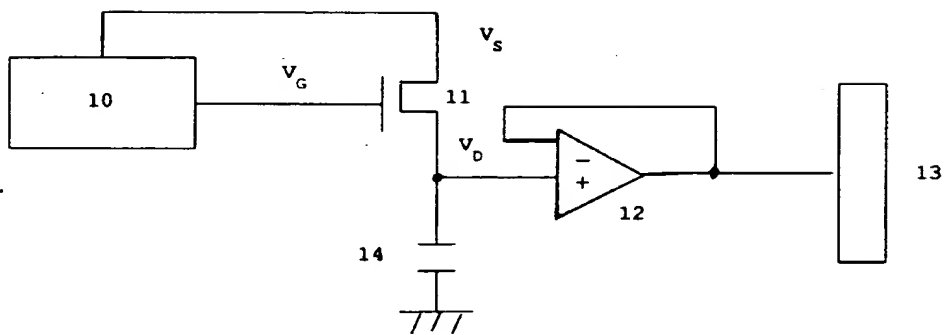


Figure 3





European Patent  
Office

# EUROPEAN SEARCH REPORT

Application Number

EP 93 10 8928

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
X	WO-A-9 204 421 (MERCK) * page 18, line 13 - page 20, line 10 * * page 31, line 24 - page 33, line 21 * * example 3 * ---	1,2,5,6,14	C09K19/54 G02F1/1333
X	WO-A-9 105 029 (MERCK) * examples 47,48 * ---	1,5,14	
P,X	EP-A-0 492 668 (SHARP CORPORATION & MERCK PATENT GESELLSCHAFT) * the whole document * ---	1,14	
A	EP-A-0 484 163 (SHARP KABUSHIKI KAISHA) * examples * ---	1,5-8,14	
A	EP-A-0 275 999 (ASAHI GLASS COMPANY) * the whole document * ---	1,4-7,9,14	
A	SPIE, LIQUID CRYSTAL DISPLAYS AND APPLICATIONS vol. 1257, 1990, pages 2 - 8 Y. HIRAI ET AL 'phase diagram and phase separation in lc/prepolymer mixture' * the whole document * ---	1,5-7,14	TECHNICAL FIELDS SEARCHED (Int. Cl.5)  C09K
A	SPIE, LIQUID CRYSTAL CHEMISTRY, PHYSICS AND APPLICATIONS vol. 1080, 1989, pages 24 - 31 F.G.YAMAGISHI ET AL. 'morphological control in polymer-dispersed liquid crystal film matrices' * the whole document * -----	1,5-7,14	
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 20 SEPTEMBER 1993	Examiner PUETZ C.
CATEGORY OF CITED DOCUMENTS			
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons * : member of the same patent family, corresponding document	